

Atty. Docket #: 1999/F-012

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

INTERNATIONAL APPL. NO.: PCT/EP00/00280 :  
INTERNATIONAL FILING DATE: 01/15/2000 :  
APPLICANT: TETSU YAMAMOTO :  
SERIAL NO: : ART UNIT:  
FILED: --HEREWITH-- : EXAMINER:  
FOR: "METHOD FOR PRODUCING :  
BRIDGED POLYMER :  
MEMBRANE AND FUEL :  
CELL" :

Commissioner for Patents  
Box PCT  
Washington, D.C. 20231

"Express Mail" No.: EK954093835

Date: --JULY 24, 2001--

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to the Commissioner for Patents, Washington, D.C. 20231

-Carrie A. McPherson-  
(Typed or printed name of mailing paper or fee)

*Carrie A. McPherson*  
(Signature of person mailing paper)

**TRANSMITTAL OF APPLICATION PAPERS  
TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371  
(37 CFR 1.494 OR 1.495)**

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

09/889971

JC18 Rec'd PCT/PTO 2 4 JUL 2001

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay.
4. ☒ A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)[2]) -- IN ENGLISH
- a. ☒ is transmitted herewith (required when not transmitted by International Bureau) --with- Two (2) Sheets of Drawings.
  - b. ☐ has been transmitted by the International Bureau. See WIPO Publication WO 00/44816.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A (verified) translation of the International Application into the English language is enclosed. (see 5. above)
7. ☐ Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)[3])
- a. ☐ are transmitted herewith (required if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
  - e. ☐ will be submitted with the appropriate surcharge.
8. ☐ A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371(c)[3]) is enclosed or will be submitted with the appropriate surcharge.

9. ☒ <sup>executed</sup> An oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371(c)[4]) will follow.  
[ ] and is attached to the translation of (or a copy of) the International Application.  
[ ] and is attached to the substitute specification.

10. ☒ A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371(c)[5]) is enclosed. (PCT/IPEA/409 & 416)

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.
12. ☒ An Assignment for recording and a separate cover sheet in compliance with 37 CFR 3.28 and 3.31 will follow.
13. ☒ A FIRST preliminary amendment is enclosed.  
A SECOND or SUBSEQUENT preliminary amendment is enclosed.
14. [ ] A substitute specification (including claims, abstract, drawing) is enclosed.
15. [ ] A change of power of attorney and/or address letter is enclosed.
16. ☒ Other items of information:

- ☒ This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of--

[ ] 22 months from the priority date under 37 CFR 1.494(c), or

☒ 32 months from the priority date under 37 CFR 1.495(c).

- ☒ The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

International Application No. PCT/EP00/00280

1999/F-012

- ☒ Receiving Office: EPO
- ☒ IPEA (if filing under 37 CFR 1.495): EPO
- ☒ Priority Claim(s) (35 USC §§ 119, 365):  
 11/018090 filed January 27, 1999 -and-  
 Japanese Appln. 11/157509 filed June 04, 1999
- ☒ A copy of the International Search Report is

☐ enclosed.

☒ attached to the copy of the International Application.

- ☒ A copy of the Receiving Office Request Form is enclosed.

- [X] Form PTO/SB/05 (1) sheet
- [X] Form PCT/IB/306 (1) sheet
- [X] Form PCT/IB/308 (1) sheet

The fee calculation is set forth on the next page of this Transmittal Letter.

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09/889971

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## FEE CALCULATION SHEET

☒ A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 860.00

Total Number of claims in  
excess of (20) times \$18..... -0-Number of independent claims  
in excess of (3) times \$80..... -0-Fee for multiple dependent  
claims \$270..... -0-TOTAL FILING FEE... \$ 860.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By Ashley I. Pezzner  
Reg. No. 35,646CONNOLLY BOVE LODGE & HUTZ LLP  
1220 Market Street  
P.O. Box 2207  
Wilmington, Delaware 19899  
Tel. (302) 658-9141

AIP/cam (8577\*36)

Enclosures

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IC18 Rec'd PCT/PTO 2 4 JUL 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: TETSU YAMAMOTO )  
)  
SERIAL NO. TO BE ASSIGNED ) ART UNIT: TO BE ASSIGNED  
)  
FILED: HERewith ) EXAMINER: TO BE ASSIGNED  
)  
FOR: METHOD FOR PRODUCING BRIDGED )  
POLYMER MEMBRANE AND FUEL CELL )

Asst. Commissioner for Patents

Washington, D.C. 20231

"EXPRESS MAIL" No. EK954093835 DATE: JULY 24, 2001

I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231

CARRIE A. MCPHERSON

(TYPED OR PRINTED NAME OF  
PERSON MAILING PAPER OR FEE)

*Carrie A. McPherson*  
(SIGNATURE OF PERSON MAILING  
PAPER OR FEE)

**PRELIMINARY AMENDMENT**

Sir:

Prior to fee calculation and examination please amend the above-identified application as follows.

**In the Claims**

Please cancel claims 2-7.

Please add the following new claims.

- 8. The method as claimed in claim 1, wherein the bridging agent has at least two epoxy groups or isocyanate groups in the molecule.
- 9. The method as claimed in claim 1, wherein the liquid medium contains 0.001 to 0.8 mole of the bridging agent per unit of the basic polymer.
- 10. The method as claimed in claim 1, wherein the basic polymer is selected from the group

consisting of polybenzimidazole, polyimidazole, polyvinylimidazole and polybenzbisimidazole.

11. The method as claimed in claim 1, further comprising the step of impregnating the basic polymer with a strong acid for providing proton conductivity.
12. The method as claimed in claim 1, wherein the basic polymer has a strong acid group in the repeating unit in the basic polymer.
13. The method as claimed in claim 8, wherein the liquid medium contains 0.001 to 0.8 mole of the bridging agent per unit of the basic polymer.
14. The method as claimed in claim 13, wherein the basic polymer is selected from the group consisting of polybenzimidazole, polyimidazole, polyvinylimidazole and polybenzbisimidazole.
15. The method as claimed in claim 1, wherein said amino group is a primary amino group or a secondary amino group.
16. The method as claimed in claim 1, wherein said basic polymer contains an aromatic ring containing at least nitrogen atom.
17. The method as claimed in claim 1, wherein said basic polymer is polybenzbisimidazole.
18. The method as claimed in claim 17, wherein a strong acid group is introduced into the amino group of a polybenzimidazole through a linker.
19. The method as claimed in claim 8, wherein the liquid medium contains 0.01 to 0.5 mole of the bridging agent.
20. The method as claimed in claim 8, wherein the liquid medium contains 0.05 to 0.3 mole of the bridging agent.

21. A fuel cell comprising a plurality of single cells, each of the single cells comprising a bridged polymer membrane obtained by the method as claimed in claim 11, and a pair of electrodes sandwiching the bridged polymer membrane.- -

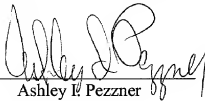
### REMARKS

The applicants respectfully request that the preliminary amendment be entered prior to fee calculation and examination. The applicants have rewritten claims 2-6 into proper U.S. form as newly added claims 8-12. Support for newly added claims 13 and 14 can be found in the original claims 3 and 4 respectively. Support for newly added claims 15 and 16 can be found in the specification at page 4, lines 4-8. Support for newly added claim 17 can be found in the original claim 4. Support for newly added claim 18 can be found in the specification at page 5, lines 11-14. Support for newly added claims 19 and 20 can be found in the specification at page 9, lines 11-14. Support for newly added claim 21 can be found in the original claim 7. No additional fee is required for the claims. If there are any additional fees due in connection with the filing of this response, the Commissioner is authorized to charge or credit any overpayment to Deposit Account No. 03-2775.

A prompt and favorable action is solicited.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

By   
 Ashley E. Pezzner  
 Reg. No. 35,646  
 Tel. (302) 888-6270

AIP/cam  
 ::ODMA\MHODMA\CB;153558;1

Method for producing bridged polymer membrane and fuel cellField of the Invention

The present invention relates to a method for producing a bridged polymer membrane and a fuel cell.

Related Art

A cell includes an electrolyte and a pair of electrodes separated by the electrolyte. In case of a fuel cell, a fuel such as a hydrogen gas is supplied to one of the electrodes, and an oxidizing agent such as an oxygen gas is supplied to the other electrode, thereby converting chemical energy involved in the oxidation of the fuel into electric energy. The electrolyte permeates hydrogen ions, that is, protons but does not permeate reactive gases such as the hydrogen gas and the oxygen gas. Typically, a fuel cell has a plurality of single cells, and each of the single cells has an electrolyte and a pair of electrodes separated by the electrolyte.

As the electrolyte for the fuel cell, a solid such as a polymer electrolyte membrane and a liquid such as phosphoric acid are used. Recently, the polymer electrolyte membranes have been receiving attention as the electrolytes for the fuel cell. For example, perfluorosulfonic acid polymers and complexes between basic polymers and strong acids are used as materials for the polymer electrolyte membranes.

Typically, the perfluorosulfonic acid polymer has a framework of perfluorocarbon such as a copolymer of tetrafluoroethylene and trifluorovinyl and a side chain being bonded thereto and having a sulfonic acid group such as a side chain that a sulfonic acid group is bonded to perfluoroalkylene group. The sulfonic acid group releases a hydrogen ion to convert into an anion, and therefore conducts proton.

Polymer electrolyte membranes comprising complexes of basic polymers and strong acids have been developed. International Publication WO96/13872 and its corresponding U.S. Pat. No. 5,525,436 disclose a method for producing a proton conductive polymer electrolyte membrane by immersing a basic polymer such as polybenzimidazoles in a strong acid such as phosphoric acid, sulfuric acid and so on. The fuel cell employing such a polymer electrolyte membrane has the advantage that it can be operated at 100 °C or above.

*J. Electrochem. Soc.*, Vol. 142, No. 7, 1995, ppL121-L123 describes that immersing

a polybenzimidazole in 11M phosphoric acid for at least 16 h impregnates five molecules of phosphoric acid per unit of the polybenzimidazole.

Further, International Publication WO97/37396 and its corresponding U.S. Pat. No. 5,716,727 describe a method for producing a polymer electrolyte membrane by obtaining a solution of a polybenzimidazole dissolved in trifluoroacetic acid, followed by adding phosphoric acid to the solution, and subsequently by removing the solvent.

The whole disclosures of WO 96/13872, *J. Electrochem. Soc.*, Vol. 142, No. 7, 1995, ppL121-L123 and WO97/37396 are incorporated herein as reference.

Even though a basic polymer by itself has a sufficient mechanical strength, there are cases that the mechanical strength of the basic polymer decreases to an insufficient degree by impregnating the basic polymer with a strong acid for providing proton conductivity. Therefore, it is desired to further improve the mechanical strength of the basic polymer for applying the complex of the basic polymer and the strong acid to the electrolyte membrane for the fuel cell and so on.

U.S. Pat. No. 5,599,639 describes a basic polymer wherein a sulfonic acid group is introduced into a basic polymer such as polybenzimidazole and so on through a linker such as an alkylene and so on. The basic polymer is required to incorporate water therein for providing proton conductivity so that the basic polymer may be used as the electrolyte membrane for the fuel cell.

However, when the basic polymer is immersed in water, there are cases that the basic polymer swells and that a sufficient mechanical strength is not achieved. The whole disclosure of U.S. Pat. No. 5,599,639 is incorporated herein as reference. The present inventors tried to improve the mechanical strength by shaping a basic polymer into a membrane configuration followed by reacting with an external bridging agent. However, the basic polymer in a gel or solid form did not smoothly react with the external bridging agent.

#### Summary of the Invention

To solve the aforementioned problem, the present invention is accomplished by shaping a basic polymer into a membrane configuration followed by proceeding a bridging reaction.

According to one aspect of the present invention, there is provided a method for producing a bridged polymer membrane, comprising the steps of: obtaining a liquid

medium comprising a basic polymer having an amino group in a repeating unit, a bridging agent, and a solvent; shaping the liquid medium into a membrane configuration to obtain a shaped membrane; and bridging the basic polymer by the bridging agent in the shaped membrane.

5 Preferably, the bridging agent has at least two epoxy groups or isocyanate groups in the molecule thereof.

Preferably, the liquid medium contains 0.001 to 0.8 mole of the bridging agent per unit of the basic polymer.

10 Preferably, the basic polymer is selected from the group consisting of polybenzimidazoles, polyimidazoles, polyvinylimidazoles, and polybenzobisimidazoles.

15 Preferably, the method may further comprise the step of impregnating the basic polymer with a strong acid for providing proton conductivity. The strong acid may be impregnated in the form of the liquid medium. Alternatively, the strong acid may be impregnated after the shaping but before the heating. Alternatively, the strong acid may be impregnated after heating.

20 Alternatively, the basic polymer may have a strong acid group in the repeating unit in the basic polymer. The presence of the strong acid provides proton conductivity.

According to another aspect of the present invention, there is provided a fuel cell comprising a plurality of single cells, each of the single cells comprising a bridged polymer membrane obtained by the aforementioned method and a pair of electrodes sandwiching the bridged polymer membrane.

#### Brief Description of the Drawings

30 Fig. 1 is a cross section of a part of a fuel cell.

Fig. 2 is an enlarged portion A of Fig. 1.

#### Preferred Embodiments of the Invention

35 The present invention may include the step of obtaining a liquid medium comprising a prescribed basic polymer, a bridging agent, and a solvent. Typically, the basic polymer is dissolved in the solvent to obtain a solution, and the bridging agent is added to the solution, followed by mixing thereof.

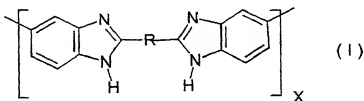
As the basic polymer, the basic polymer including an amino group in a repeating unit is used. Since the amino group is present in the repeating unit, the polymer becomes basic and the amino group may react with the bridging agent. In view of the reactivity with the bridging agent, the amino group in the repeating unit is preferably a primary amino group or a secondary amino group.

The repeating unit in the basic polymer preferably contains an aromatic ring containing at least one nitrogen atom. The aromatic ring is preferably a five-membered ring or a six-membered ring containing one to three nitrogen atoms, which may be fused with another ring, particularly another aromatic ring.

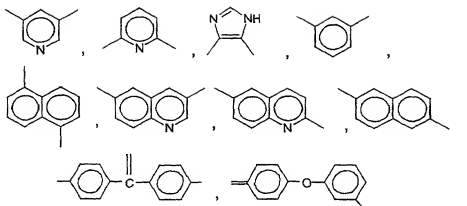
Preferably, the basic polymer is soluble to the solvent. Specifically, a solution preferably dissolves not less than 1 percent by weight of the basic polymer and further preferably not less than 2 percent by weight. The features facilitates forming a uniform polymer membrane without forming pores therein.

The basic polymer which may be used in accordance with the present invention includes polybenzimidazoles, polyimidazoles, polyvinylimidazoles, and polybenzbisimidazoles. Among these, polybenzimidazoles are preferable.

As for the polybenzimidazoles, those of the following formula are preferably used:

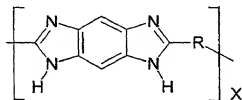


wherein R represents alkylene, perfluoroalkylene, or a substituent of any of the following formulae:



further wherein each of alkylene and perfluoroalkylene groups, which may be R, has 1 to 10 carbons preferably, and more preferably 1 to 6 carbons.

Furthermore, the basic polymers which may also be used are polybenzbisimidazoles of the following formula:



wherein R has the aforementioned meaning.

A strong acid group such as a sulfonic acid group( $-\text{SO}_3\text{H}$ ), a phosphate monoester group( $-\text{O}-\text{P}(=\text{O})(\text{OH})_2$ ) and so on may be introduced into the amino group of the polybenzimidazoles or the polybenzobisimidazoles through a linker.

As for the linker, the aforementioned R may be used. Alternatively, the linker may include a linear or branched hydrocarbon group having 1 to 20 carbon atoms, which may be substituted with a fluorine atom, which may be interrupted by an oxygen atom (-O-) or a group represented by a formula  $-N(R^2)-$  wherein  $R^2$  is a hydrogen atom or a lower alkyl group having 1 to 6 carbon atoms. The hydrocarbon group includes: a lower alkylene group having 1 to 20 carbon atoms, which may be interrupted by an oxygen atom or an arylene group such as a phenylene group, and which may be branched; and an arylene group such as a phenylene group, which may be substituted with a lower alkyl group, a lower alkoxy group, a sulfonic acid group, an amino group, a fluorine atom and so on. Alternatively, a group represented

by a formula  $-(CR^3R^4)_p-O-(CR^5R^6)_q-$

wherein p and q are independent, and each is an integer of 1 to 10; and

$R^3$ ,  $R^4$ ,  $R^5$ , and  $R^6$  are independent, and each is the same or different and a hydrogen atom; a fluorine atom; a lower alkyl group or a lower alkoxy group having 1 to 6 carbon atoms; an aryl group such as a phenyl group which may be substituted with a lower alkyl group, a lower alkoxy group, a sulfonic acid group, an amino group, a fluorine atom and so on; or a strong acid group such as a sulfonic acid group, a phosphate monoester group, and preferably a hydrogen atom; a fluorine atom; or a lower alkyl group having 1 to 6 carbon atoms.

For example, a group represented by a formula  $>N-(CR^3R^4)_r-SO_3H$  wherein N represents a nitrogen atom in the imidazole ring of the polybenzimidazoles or the polybenzobisimidazoles; r is an integer of 1 to 20; and  $R^3$  and  $R^4$  have the aforementioned meanings may be introduced into the polybenzimidazoles or the polybenzobisimidazoles.

When a strong acid group is introduced into the nitrogen atom of the polybenzimidazoles or the polybenzobisimidazoles through the linker, it is not necessary that the linker and the strong acid are introduced into all of the nitrogen atoms. The linker and the strong acid may be introduced into some of the nitrogen atoms, and hydrogen atoms may remain bonded to the other nitrogen atoms. The remaining nitrogen atoms may be reacted with the bridging agent, and therefore it is preferable.

For example, the linker and the strong acid may be introduced into 5 to 85 percent of the nitrogen atoms of the basic polymer such as the nitrogen atoms of the imidazole ring, and particularly, the linker and the strong acid may be introduced into 10 to 75 percent of the nitrogen atoms, and further particularly, the linker and the strong acid may be introduced into 15 to 40 percent of the nitrogen atoms.

The basic polymer may be reacted with a sulfone in a solution of the basic polymer to sulfonate or sulfoalkylate the basic polymer. In the reaction, for example, a solution of 1 to 30 percent by weight of the basic polymer may be used, and particularly, a solution of 5 to 20 percent by weight of the basic polymer may be used. As for the solvent for the sulfonation or sulfoalkylation, the solvent for the liquid

medium, which will be described later, is preferably used.

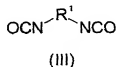
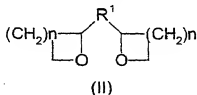
The reaction is, for example, described in U.S. Pat. No. 5,599,639, U.S. Pat. No. 4,814,399 and Ahmed Mstafa, Chemical Review, pp. 195-223(1954), and these documents are incorporated herein as reference.

As the solvent used for the liquid medium, the solvent that does not react with the bridging agent is preferable. An organic solvent is preferable, and an organic solvent having polarity is further preferable. The organic solvent includes, for example, lower amides such as N-methyl-2-pyrrolidone, N, N-dimethylacetamide, dimethylformamide; dimethylsulfoxide and so on. A mixture of these solvents may be used.

The liquid medium may be either a solution or a suspension. In case of the solution, the basic polymer is dissolved in the solvent. In case of the suspension, particles of the basic polymer serving as a dispersion phase is dispersed in a solvent serving as a continuous phase. Alternatively, the liquid medium may be a slurry or a paste.

The bridging agent is not limited as long as the bridging agent includes a compound having a functional group reacting with an amino group. The bridging agent preferably has at least two functional groups for reacting with the amino group in the molecule thereof, and the bridging agent is typically an organic compound. Examples of such functional groups include epoxy groups and isocyanate groups. However, when the epoxy group and the isocyanate group are present in the molecule of the bridging agent, both groups react each other and therefore, it is not preferable.

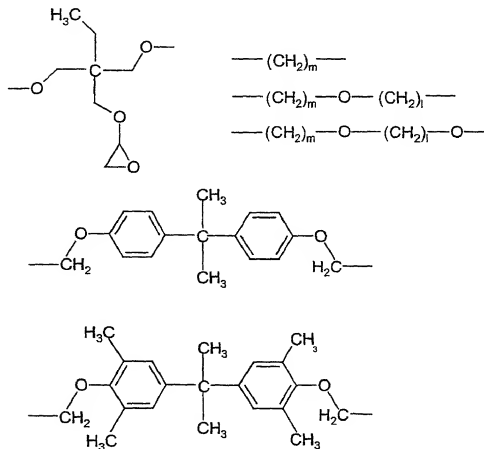
The organic compound having not less than two epoxy groups and not less than two isocyanate groups includes, for example, an epoxy compound represented by formula (II), and an organic compound represented by formula (III). Further, the hydrogen atoms in the epoxy groups of the epoxy compound represented by formula (II) may be substituted by a halogen or a lower alkyl group.



In the aforementioned formula,  $\text{R}^1$  is a hydrocarbon group, including, for example, a linear chain or branched lower alkylene group which may be substituted by a nitro

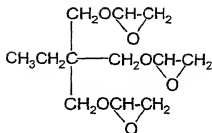
group, an oxygen atom, an epoxy group or an aryl group; and a linear chain or branched lower alkoxy group which may be substituted with a nitro group, an epoxy group or an aryl group. As for the aryl group, a phenyl group, a naphthalenyl group and an indenyl group can be mentioned.  $n$  is an integer of 0 or 1, and preferably 0.

Examples of  $R^1$  include the following groups.



In the aforementioned formulae,  $m$  and  $l$  are the same or different and each is an integer of 1 to 6.

An example of the bridging agent having three functional group in the molecule, which reacts with an amino group is shown as follows.



Preferably, the liquid medium contains at least 1 percent by weight of the basic polymer, and further preferably, the liquid medium contains at least 2 percent by weight of the basic polymer. Preferably, the liquid medium contains not more than 95 percent by weight of the basic polymer, and further preferably, the liquid medium contains not more than 80 percent by weight of the basic polymer, and particularly preferably, the liquid medium contains not more than 50 percent by weight of the basic polymer.

Preferably, the liquid medium contains 0.001 to 0.8 mole of the bridging agent per unit of the basic polymer, and further preferably, the liquid medium contains 0.01 to 0.5 mole of the bridging agent, and particularly preferably, the liquid medium contains 0.05 to 0.3 mole of the bridging agent. When an amount of the bridging agent is too much, it becomes difficult to impregnate a strong acid in the basic polymer. On the other hand, when an amount of the bridging agent is too small, the mechanical strength of the polymer membrane is not sufficiently improved.

Subsequently, the liquid medium is shaped into a membrane configuration to obtain a shaped membrane. For example, the liquid medium is cast onto a planar substrate, and then dried in a reduced pressure. Alternatively, the basic polymer may be shaped into the membrane configuration by a doctor-blade method.

The substrate for the casting or the doctor-blade method may be a semiconductor such as a silicon wafer, a synthetic polymer such as poly(ethyleneterephthalate), and a metal such as a stainless steel. When a roll made of, for example, poly(ethyleneterephthalate) is used as the substrate, a continuous castor may be used to produce a shaped membrane having a constant width and any thickness. In this case, the liquid medium is cast onto the substrate, and go through a gap having a prescribed distance, and then go through a drying furnace for drying by a warm wind.

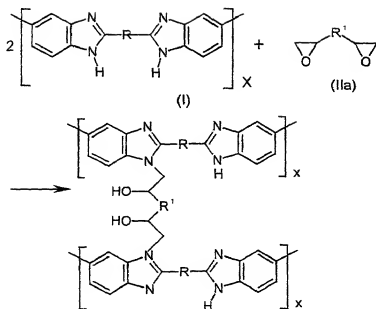
Alternatively, the basic polymer may be shaped into the membrane configuration according to the method as described in Japanese Patent Appln. Hei 10-125560, filed May 8, 1998: entitled "Method for Producing Polymer Electrolyte Membrane for Fuel Cell and Fuel Cell." Specifically, the liquid medium is poured into a cylinder having the inner surface having a cylindrical configuration, and subsequently, the cylinder is rotated. At that point, the solvent is allowed to evaporate through centrifugal force by the rotation; concurrently, a polymer membrane having a cylindrical configuration of substantially uniform thickness is formed on the inner surface of the cylinder. Thereafter, the polymer membrane having a cylindrical configuration is cut out to yield a shaped membrane having a membrane configuration. This method allows to form the basic polymer having a uniform matrix. The disclosure of Japanese Patent Appln. Hei 10-125560 is incorporated herein as reference.

In the present invention, the basic polymer is bridged by the bridging agent in the shaped membrane. Typically, the shaped membrane is heated to bridge the basic polymer by the bridging agent. However, it is not limited to heating, and a photochemical reaction may bridge the basic polymer by the bridging agent.

In the following description, an embodiment that the bridging agent is reacted by heating is mainly described. The aforementioned shaping step, in many cases, may include the step of heating the membrane for drying the shaped membrane. The heating for drying may form the shaped membrane and simultaneously bridge the basic polymer by the bridging agent in the basic polymer. To facilitate drying, it may be heated in a reduced pressure of not more than 1 atmospheric pressure, preferably not more than 0.1 atmospheric pressure and further preferably not more than 0.05 atmospheric pressure.

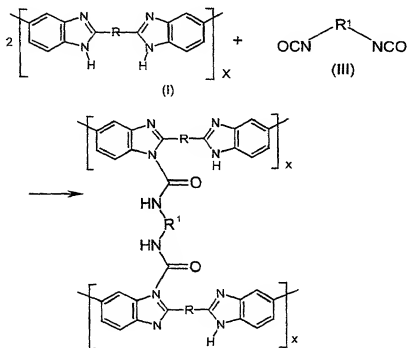
Alternatively, the heating for drying the shaped membrane may be determined to a temperature which is lower than the reaction temperature of the bridging agent, and subsequently, the shaped membrane may be distinctly heated for bridging the bridging agent. A warm wind may be used for the heating for drying or the heating for bridging.

For example, the epoxy compound represented by formula (IIa) is reacted with polybenzimidazole represented by formula (I) to bridge a polymer chain.



In the aforementioned formulae, R<sup>1</sup> is the same as defined above.

Similarly, the isocyanate compound represented by formula (III) is reacted with polybenzimidazole represented by formula (I) to bridge a polymer chain.



In the aforementioned formulae, R<sup>1</sup> is the same as defined above.

In the aforementioned formulae, it is described such that different polymer chains are

bridged for convenience of the description. However, the same polymer chain may be bridged, and an inside of one repeated unit may be bridged.

In the present invention, preferably, the step of impregnating the basic polymer with a strong acid for providing proton conductivity may be included. The strong acid may be impregnated in the form of the liquid medium. Alternatively, the strong acid may be impregnated after the shaping but before the heating. Alternatively, the strong acid may be impregnated after heating.

The embodiment that strong acid is impregnated in the form of the liquid medium refers to adding a strong acid to the liquid medium. Preferably, the bridging agent does not react with the strong acid.

Preferably, the strong acid may be impregnated after heating the shaped membrane. The bridged, basic polymer has improved mechanical strength, and the handling thereof is easier. Since the bridging agent is already reacted, and therefore, the reaction of the strong acid with unreacted bridging agent is very limited.

The bridged, basic polymer membrane may be immersed in the strong acid so that the strong acid is impregnated in the basic polymer membrane. The basic polymer may be immersed in a strong acid having a high concentration at a temperature of not less than 35°C, preferably not less than 40°C, further preferably not less than 50°C for a period of not more than 5 hours, preferably not more than 1 hour. By carrying out the immersion step at 35°C or above, it becomes possible to shorten the time for immersing the basic polymer in the strong acid. However, in view of the stability of the basic polymers and the safety precautions required to handle the strong acids at high temperatures, preferably, the immersion step is carried out at not more than 200°C or below, more preferably at 100°C or below, and most preferably at 80°C or below.

Protic strong acids may be used as the strong acid. For example, phosphoric acid and sulfuric acid are preferably used.

As used in the present specification, the "phosphoric acid" includes phosphorous acid ( $\text{H}_3\text{PO}_3$ ), orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ), pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ), triphosphoric acid ( $\text{H}_5\text{P}_3\text{O}_{10}$ ), and metaphosphoric acid. The phosphoric acid, particularly orthophosphoric acid, preferably has a concentration of not less than 80 percent by weight; more preferably, a concentration of not less than 90 percent by weight; even more preferably, a concentration of not less than 95 percent by weight;

and most preferably, a concentration of not less than 98 percent by weight. This is because the basic polymer can be impregnated with a larger number of strong acid molecules as the concentration of the strong acid increases.

5 The polymer electrolyte membrane obtained by the present invention, namely, the complex between the basic polymer and the strong acid, is proton conductive, and therefore, it may preferably be used as an electrolyte for cells. Nevertheless, the polymer electrolyte is not be limited to its use for the cell; but it can also be used as the electrolyte for a display element, an electrochromic element or a various sensor.

10 According to another aspect of the present invention, the polymer electrolyte membrane can preferably be used in the single cell for a fuel cell.

15 In referring to Fig. 1, the single cell for a fuel cell 10 has a polymer electrolyte membrane 12 and a pair of electrodes 20 sandwiching the polymer electrolyte membrane 12. Each of the electrode 20 has a catalytic layer 14 and a gas diffusion layer 22 for supplying a reaction gas with the catalytic layer 14.

20 In Fig. 2, the catalytic layer 14 has a matrix 15 consisting essentially of a polymer electrolyte membrane and a plurality of catalytic particles 16 being dispersed in the matrix. The matrix 15 along with the polymer electrolyte membrane 12 forms a channel for conducting hydrogen ions. The material for the matrix 15 is preferably the same as the material for the polymer electrolyte membrane 12. However, these materials may be different. The matrix 15 may be porous so as to allow the reactive gas to pass through. The catalytic particles preferably contact each other, thereby forming a channel for conducting electrons.

25 Each of the catalytic particles 16 has an electrically conductive carrier 17 and a catalytic substance 18 being loaded onto a surface of the electrically conductive carrier 17. The electrically conductive carrier may be carbon particles. The catalytic substance 18 may be platinum metal or a platinum alloy. In Fig. 2, the catalytic substance 18 is coated onto the surface of the electrically conductive carrier 17. Alternatively, the catalytic substance 18 may have a particle configuration.

30 The gas diffusion layer 22 is porous so as to allow the reactive gas to pass through. In Fig. 2, the gas diffusion layer 22 is made of a plurality of electrically conductive particles 26 forming a gap 24. The electrically conductive particles may be carbon particles and same as electrically conductive carrier 17. Alternatively, the electrically

conductive particle 26 is replaced by electrically conductive substance such as carbon fibers.

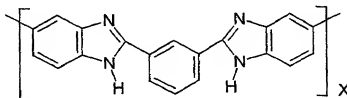
The polymer electrolyte membrane in accordance with the present invention may be used as the electrolyte membrane 12. Moreover, the electrolyte membrane 12 as well as a precursor for a single cell having one of or both catalytic layers 14 may be produced. Furthermore, the single cell may be produced by fixing the gas diffusion layer 22 to the precursor.

### Examples

The following examples are merely illustrative of the present invention, and are not to be construed as limitations thereof.

#### Example 1

Polybenzimidazole having the structural formula described below and having an intrinsic viscosity of 1.1 (available from Hoechst Celanese Inc.) was dissolved in N,N-dimethylacetamide to yield a solution having a resin concentration of 10 percent by weight.



Subsequently, an amount shown in Table 1 of ethyleneglycoldiglycidylether as a bridging agent is added to the solution and mixed thereof. The mixed solution thus obtained was cast onto a 6-inch silicon wafer, and dried at 90 °C for four hours in a reduced pressure (10 mmHg) for forming a membrane and for proceeding the bridging reaction at the same time to obtain a cast film having a thickness of about 50 micrometer. The film thus obtained is flexible compared to unbridged polybenzimidazoles. The solubility of the cast film at room temperature in N,N-dimethylformamide was determined. The results are shown in Table 1.

Table 1

Sample	Added Amount of Ethyleneglycoldiglycidylether (molar percent)	solubility in N,N-dimethylacetamide
1	100	insoluble, no swelling
2	50	insoluble, no swelling
3	15	insoluble, swelling
4	10	insoluble, swelling
5	5	insoluble, swelling considerably
6	0	soluble

## Example 2

The bridged polybenzimidazole obtained in Example 1 (50 micrometer thickness) was cut out in 3-cm square pieces. The films were washed with water to wash away the remaining N,N-dimethylacetamide. Then, they were dried at a reduced pressure and the weights of the films were measured.

Thereafter, the dried polybenzimidazole films were placed in sample vials. To each of these was added 30 ml of 85 percent by weight aqueous orthophosphoric acid, and then immersed at room temperature for 72 hours. Subsequently, the polybenzimidazole films impregnated with orthophosphoric acid were removed from the phosphoric acid, and excess phosphoric acid on their surfaces was thoroughly wiped off with filter papers. Subsequently, the weight increments were determined by weighing. After weighing, the polybenzimidazole films were placed in 1-liter volumetric flasks, and deionized water was filled up to the measuring lines and stirred. Orthophosphoric acid was extracted from the polybenzimidazole films to obtain aqueous phosphoric acid solutions. The aqueous phosphoric acid solutions thus obtained were titrated with 0.02 N sodium hydroxide solution, and the quantities of orthophosphoric acid being impregnated in the polybenzimidazole films were determined. The difference between the weight increment after impregnation with orthophosphoric acid and the weight of orthophosphoric acid of impregnation was calculated to be the quantity of the water that had been adsorbed to each polybenzimidazole film impregnated with orthophosphoric acid. These results are shown in Table 2.

Table 2

Sample	Added Amount of Ethyleneglycol-diglycidylether (molar %)	Number of phosphoric acid molecules impregnated per repeating unit of the polymer	Number of water molecules impregnated per repeating unit of the polymer
1	100	0	---
2	50	0	---
3	15	6.59	9.83
4	10	6.61	11.83
5	5	7.74	13.08

The results show that the bridged polymer membranes that is impregnated with orthophosphoric acid are obtained. Therefore, such polymer membrane may be sued as an electrolyte membrane for a fuel cell.

Even though an added amount of the bridging agent is at least 50 percent by mole, it is possible to impregnate phosphoric acid by increasing temperatures of the phosphoric acid to 50 °C. However, in this case, it takes at least seven days for impregnation, and the mechanical strength after impregnation decreases, and the film became brittle.

### Example 3

Polybenzimidazole having the structural formula described in Example 1 and having an intrinsic viscosity of 1.1 (available from Hoechst Celanese Inc.) was dissolved in N,N-dimethylacetamide to yield a solution having a resin concentration of 10.0 percent by weight. Subsequently, 10 percent by mole based on a unit of polybenzimidazole of ethyleneglycoldiglycidylether as a bridging agent is added to the solution and mixed thereof.

65 gram of the solution was introduced into a stainless- steel cylinder having a cylindrical configuration with an inner diameter of 141 millimeter and a length of 408 millimeter. The cylinder was rotated at 90°C for two hours at 2500 rpm to obtain a bridged membrane of polybenzimidazole having a cylindrical configuration. A thickness of the polybenzimidazole membrane was determined at any six points. An

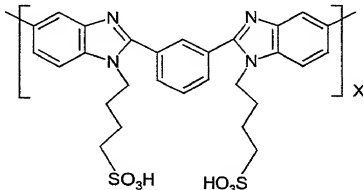
average of the thickness was 47 micrometers.

#### Example 4

A polybenzimidazole bridged membrane of Example 3 was immersed in 85 percent by weight phosphoric acid at room temperature for 96 hours to yield a polymer electrolyte membrane. This polymer electrolyte membrane was cut out in a circular piece. Next, it was sandwiched by two sheets of carbon electrodes for a fuel cell of the polymer electrolyte type, which were commercially available, and hot-pressed at 140 °C and 50 kgf/cm<sup>2</sup> (1 kgf is equivalent to about 9.8 Newton) to yield a single cell for fuel battery. When hydrogen and air were introduced into this single cell for generating electricity, following outputs were obtained: 300 mW/ cm<sup>2</sup> at 160 °C and 0.5 V under 1 atmospheric pressure, and 475 mW/ cm<sup>2</sup> at 160 °C and 0.5 V under 3 atmospheric pressures, respectively.

#### Comparative Example 1

Polybenzimidazole having a sulfobutylene group  $-(CH_2)_4-SO_3H$  in a side chain was prepared in a method of Example 1 of U.S. Pat. 5,599,639. Namely, polybenzimidazole having the following repeating unit was prepared.



Poly 2,2'-(m-phenylene)-5,5'-bibenzimidazole was dissolved in N-methyl-2-pyrrolidone, and then lithium hydride was added to the solution. Subsequently, the solution was heated to 70 °C for 12 hours under stirring. After the bubbling ceased, a mixture of 9 parts by mole of 1,4-butanediol and N-methyl-2-pyrrolidone were added dropwise by an addition funnel. Subsequently, the solution was further heated to 70 °C for 12 hours under stirring. Thus, poly 2,2'-(m-phenylene)-N,N'-sulfobutylene-5,5'-bibenzimidazole having a sulfonation rate of 70.5 percent was obtained.

The polymer was dissolved in dimethylsulfoxide to obtain a polymer solution having a polymer concentration of 5 percent by weight. The solution was cast onto a 6-inch silicon wafer, and dried at 90 °C for four hours in a reduced pressure (10 mmHg) for forming a membrane and for proceeding the bridging reaction at the same time to obtain a cast film. When the cast film thus obtained was immersed in pure water, the cast film considerably swelled so that the film configuration was not kept. The film could not be recovered from the water.

#### Example 5

To 15 gram of the polymer solution of Comparative Example 1 was added 0.0912 gram of ethyleneglycoldiglycidylether, and mixed thereof. In the solution, a molar ratio of the unsubstituted imidazole group to ethyleneglycoldiglycidylether was about 2:1. The mixed solution thus obtained was cast onto a 6-inch silicon wafer, and dried at 90 °C for four hours in a reduced pressure (10 mmHg) for forming a membrane and for proceeding the bridging reaction at the same time to obtain a cast film. When the cast film thus obtained was immersed in pure water, the film swelled, and it was easily peeled off from the silicon wafer while the film kept the film configuration. A thickness during containing water was about 65 micrometer.

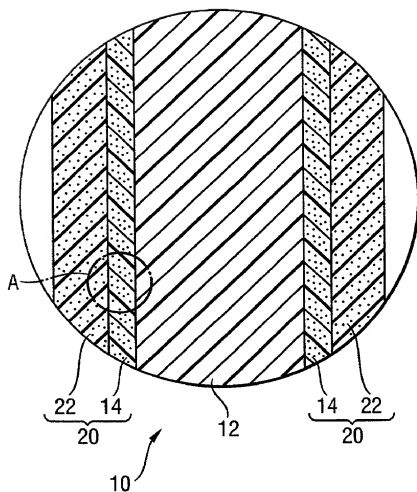
The proton conductivity of the bridged, butylsulfonated polybenzimidazole thus obtained in water was measured by a complex impedance process, and it was 51 mS/cm at 25°C and 118 mS/cm at 57°C.

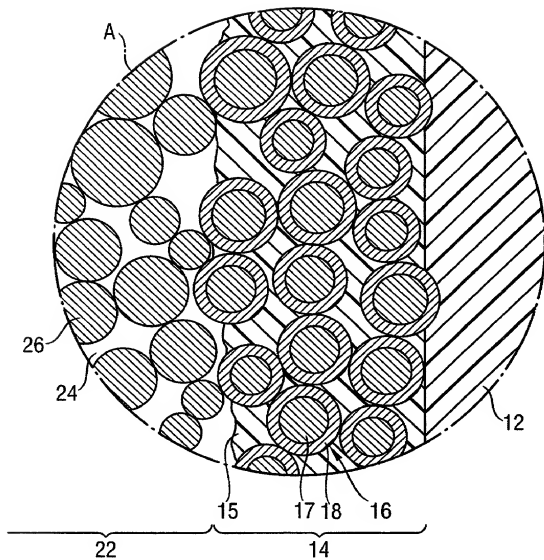
Therefore, it is confirmed that the present invention may be applied to a basic polymer having proton conductivity.

In the present invention, shaping a basic polymer into a membrane configuration and then proceeding a bridging reaction allow to improve the mechanical strength of the basic polymer. Adjusting an amount of the bridging agent allows to maintain a capacity of the basic polymer to impregnate a strong acid.

## Claims:

1. A method for producing a bridged polymer membrane, comprising the steps of:
- 5 obtaining a liquid medium comprising a basic polymer having an amino group in a repeating unit, a bridging agent, and a solvent;  
shaping the liquid medium into a membrane configuration to obtain a shaped membrane; and  
bridging the basic polymer by the bridging agent in the shaped membrane.
- 10 2. A method of claim 1 wherein the bridging agent has at least two epoxy groups or isocyanate groups in the molecule thereof.
3. A method of claim 1 or 2 wherein the liquid medium contains 0.001 to 0.8 mole of the bridging agent per unit of the basic polymer.
- 15 4. A method of claim 1, 2 or 3 wherein the basic polymer is selected from the group consisting of polybenzimidazoles, polyimidazoles, polyvinylimidazoles, and polybenzbisimidazoles.
- 20 5. A method of claim 1 further comprising the step of impregnating the basic polymer with a strong acid for providing proton conductivity.
6. A method of claim 1 wherein the basic polymer has a strong acid group in the repeating unit in the basic polymer.
7. A fuel cell comprising a plurality of single cells, each of the single cells comprising a bridged polymer membrane obtained by a method of claim 5 or 6 and a pair of electrodes sandwiching the bridged polymer membrane.
- 30

***Fig. 1***

**Fig. 2**



1999/F012 US PCT

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**Method for producing bridged polymer membrane and fuel cell**

the specification of which

- is attached hereto

- was filed on January 15, 2000 as International Patent Application PCT/EP00/00280 and including all the amendments through the date hereof.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

**Prior Foreign Application(s) for which Priority is Claimed:**

Japan, 11-018090 of January 27, 1999

Japan, 11-157509 of June 4, 1999

And I hereby appoint

Rudolf E. Hutz, Reg.No. 22,397; Harold Pezzner, Reg.No. 22,112; Richard M. Beck, Reg.No. 22,580; Paul E. Crawford, Reg.No. 24,397; Thomas M Meshbesher, Reg.No. 25,083; Robert G. McMorrow, Jr., Reg.No. 30,962; Patricia Smink Rogowski, Reg.No. 33,791; Ashley I. Pezzner, Reg.No. 35,646; William E. McShane, Reg. 32,707; James T. Moore, Reg. No. 35,619; Mary W. Bourke, Reg.No. 30,982; Gerard M. O'Rourke, Reg.No. 39,794; Christine M. Hansen, Reg.No. 40,634; Allan N. Kutzenco, Reg. No. 38,945; James M. Olsen, Reg.No. 40,408; Francis DiGiovanni, Reg.No. 37,310; Frank Z. Yang, Reg. No. 35,417; Eric J. Vain, Reg.No. 42,517; Daniel C. Mulveny, Reg.No. P-45,897; and Elliot C. Mendelson, Reg.No. 42, 878

all of CONNOLLY AND HUTZ, P.O.Box 2207, Wilmington, Delaware 19899-2007, my attorneys with full power of substitution, to prosecute this application, and transact all business in the Patent and Trademark Office connected therewith and I hereby request that all correspondence in this application be directed to:

**CONNOLLY AND HUTZ  
P.O.Box 2207  
Wilmington, Delaware 19899  
Telephone (302) 658-9141**

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00  
INVENTOR(S) / Residence

1) Tetsu Yamamoto 11-27-405, Higashi-Tamachi, Kawagoe-shi, Saitama 350-1114, Japan JPX

Signature:

Tetsu Yamamoto

Date:

July 27, 2001

The inventor is citizen of Japan.

Post Office Address of all Inventors:

Celanese Ventures GmbH  
Intellectual Property Group,  
Industriepark Höchst, Geb. K801  
65926 Frankfurt  
Germany